PRODUCTION OF PDMS/PVDF THIN FILM COMPOSITE MEMBRANE FOR CO_2/N_2 SEPARATION

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ABSTRACT

In this thesis, a thin film composite (TFC) membrane was prepared for separation of carbon dioxide (CO_2) and nitrogen (N_2). The main purpose of this research is to study the performance of polydimethyl siloxane (PDMS)/polyvinylidene fluoride (PVDF) thin film composite membrane in term of permeability and selectivity. The support layer was fabricated from PVDF and the coating layer was prepared from PDMS at various concentrations which are 3, 5, 8 and 10 wt. % PDMS. The coating of the membrane was done by the dip coating method. The permeations and selectivity of the prepared membranes for CO_2 and N_2 was tested using gas permeation test under the pressure up to 2 bars. Parameters such as the concentration of PDMS on the coating layer and various feed pressures that influence the performances of the membranes were evaluated. The results indicated that the permeability of the membranes is decrease with increment of the concentration of PDMS on the coating layer but increase in term of selectivity. The test also shows the correlation between the feed pressure applied and the performance of the membrane. Increment in the feed pressure is increasing the selectivity and permeability of the membranes. The morphology of the membrane is characterized using Scanning Electron Microscopy (SEM) and the chemical component of the membrane is analysed by Fourier Transforms Infrared (FTIR). The analysis from the membrane characterization is supporting the performance of the membrane. Membrane with 10 wt. % PDMS concentration shows the best performance with high feed pressure.

ABSTRAK

Membran filem nipis komposit telah dihasilkan dalam kajian ini untuk prosess pengasingan di antara gas karbon dioksida (CO_2) dan gas nitrogen (N_2). Tujuan utama kajian ini adalah untuk mengkaji prestasi membran polydimethylsiloxane (PDMS)/ fluoride polyvinylidene (PVDF) filem nipis komposit dalam jangka kebolehtelapan dan kemampuan pemilihan gas. Lapisan sokongan dibuat daripada PVDF dan lapisan salutan disedia dari PDMS pada kepekatan yang berbeza iaitu 3, 5, 8 dan 10 wt. % PDMS. Lapisan salutan membran dilakukan mengikut kaedah salutan berendam. Kebolehtelapan dan kebolehpilihan membrane yang telah siap untuk CO_2 dan N_2 telah diuji dengan menggunakan ujian penyerapan gas di bawah tekanan 1 dan 2 bar. Parameter seperti kepekatan PDMS pada lapisan salutan dan pelbagai tekanan suapan yang mempengaruhi prestasi membrane dinilai. Keputusan menunjukkan bahawa kebolehtelapan membran menurun dengan kenaikan kepekatan PDMS pada lapisan salutan tetapi peningkatan dalam tempoh pemilihan. Ujian ini juga menunjukkan kaitan antara tekanan suapan yang dikenakan dan prestasi membran. Kenaikan dalam tekanan suapan meningkatkan pemilihan dan kebolehtelapan membran. Morfologi membran dicirikan menggunakan Microscopy Imbasan Elektron (SEM) dan komponen kimia selaput dianalisis oleh Fourier mengubah Infrared (FTIR). Analisis daripada pencirian membran menyokong prestasi membran. Membran dengan berat 10. % Kepekatan PDMS menunjukkan prestasi terbaik dengan tekanan suapan yang tinggi.

TABLE OF CONTENT

CHAPTER	TITLE	Pages
	SUPERVISOR'S DECLARATION	ii
	STUDENT'S DECLARATION	iii
	ACKNOWLEDGEMENT	v
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENTS	viii
	LIST OF TABLES	xi
	LIST OF FIGURES	xi
	LIST OF SYMBOLS	xiii
	LIST OF ABBREVIATIONS	xiv
1	**INTRODUCTION**	
	1.1 Background of Research	1
	1.2 Problem Statement	3
	1.3 Research Objective	3
	1.4 Scope of Research	4
	1.5 Significance of Research	4

2 LITERATURE REVIEW

2.1 Membrane 5

2.1.1 Definition 5
2.1.2 Principal 5
2.1.3 Types of Membrane 7
2.1.4 Membrane of Structure 9
2.1.5 Mechanism of Membrane 10

2.2 Membrane Process 11

2.3 Membrane Module 13

2.3.1 Plate and Frame Module 13
2.3.2 Spiral Wound Module 13
2.3.3 Tubular Module 14
2.3.4 Capillary Module 15
2.3.5 Hollow Fibre Module 16

2.4 Application of Membrane 17

2.4.1 Wastewater Treatment 17
2.4.2 Gas Separation 19

2.5 Gas Separation System 19

2.5.1 Water and Polyethylene Glycol Scrubbing 20
2.5.2 Chemical Absorption 21
2.5.3 Pressure Swing Adsorption 22
2.5.4 Cryogenic Separation 23
2.5.5 Membrane Separation 24

2.6 Polymeric Membrane 26

2.6.1 Glassy Polymer 26
2.6.2 Rubbery Polymer 26

2.7 Membrane Material 27

2.7.1 Polydimethylsiloxane (PDMS) 27
2.7.2 Polyvinylidene fluoride (PVDF) 30

2.8 Thin Film Composite (TFC) 32

3	**METHODOLOGY**	
	3.1 Research Design	34
	3.2 Coating layer Selection	36
	3.2.1 Polydimethylsiloxane (PDMS)	36
	3.3 Solvent Selection	37
	3.3.1 n-hexane	37
	3.4 Penetrants	38
	3.5 Thin Film Composite (TFC) Formation	38
	3.6 Gas Permeation Test	39
	3.7 Membrane Characterization	41
	3.7.1 Scanning Electron Microscopy (SEM)	41
	3.7.2 Fourier Transfer Infrared (FTIR) Spectroscopy	43
4	**RESULTS AND DISSCUSSION**	
	4.1 Introduction	44
	4.2 Gas Permeation Result	45
	4.3 Scan Electron Microscopy (SEM) Analysis	49
	4.4 Relationship of Membrane Performance with Membrane Morphology	53
	4.5 Fourier Transfer Infrared (FTIR) Analysis	55
5	**CONCLUSION AND RECOMMENDATIONS**	
	5.1 Conclusion	60
	5.2 Recommendations	61
6	**REFERRENCES**	62

LIST OF TABLES

Table No.	Title	Page
Table 2.1	Membrane separation process	12
Table 2.2	Characteristics of major module membrane	17
Table 2.3	Process and membrane characteristics in wastewater treatment	18
Table 2.4	Gas separation and application	19
Table 2.5	Advantages and disadvantages of gas system technology	25
Table 2.6	Properties of Polydimethylsiloxane (PDMS)	28
Table 2.7	Gas permeabilities of gas separation polymers	29
Table 2.8	General properties of Polyvinylidene fluoride (PVDF)	31
Table 3.1	Characteristics of PDMS	36
Table 3.2	Characteristics of n-hexane	37
Table 3.3	Characteristics of penetrants	38
Table 4.1	Pressure normalized flux and selectivity of each membrane from Gas Permeation Test	43
Table 4.2	Infrared characteristics absorption of PDMS	55

LIST OF FIGURES

Figure No.	Title	Page
Figure 2.1	Schematic diagram of membrane separation	6
Figure 2.2	Feed flow illustration	7
Figure 2.3	Membrane classification according to morphology	9
Figure 2.4	Illustration on membrane mechanism	11
Figure 2.5	Schematic diagram for plate and frame module	13
Figure 2.6	Spiral wound membrane module	14
Figure 2.7	Schematic diagram of tubular membrane module	14
Figure 2.8	Schematic diagram of capillary membrane	15
Figure 2.9	Hollow fibre membrane module	16
Figure 2.10	Flow diagram of water scrubbing system	20
Figure 2.11	Flow diagram of chemical absorption process	21
Figure 2.12	Schematic diagram of pressure swing adsorption process	22
Figure 2.13	Flow diagram for cryogenic separation process	23
Figure 2.14	Schematic diagram for gas separation using membrane	24
Figure 2.15	Thin film composite (TFC) membrane structure	33
Figure 3.1	Research design flowchart	35
Figure 3.2	Schematic diagram of experimental setup for gas permeation test	39
Figure 3.3	Schematic diagram for membrane cell	39
Figure 3.4	Schematic diagram of Scanning Electron Microscopy (SEM)	42
Figure 3.5	Image of Fourier Transfer Infrared (FTIR) Spectroscopy	43
Figure 4.1	Relationship between permeance, GPU and coating layer concentration, wt.% at different pressure applied for carbon dioxide (CO_2)	46
Figure 4.2	Relationship between permeance, GPU and coating layer concentration, wt.% at different pressure applied for carbon dioxide (N_2)	47
Figure 4.3	Relationship between selectivity and coating layer concentration at different pressure	48
Figure 4.4	Cross Section of membrane with different concentration	50
Figure 4.5	Surface view for different concentration of PDMS	52
Figure 4.6	Infrared spectrum of 3 wt. % PDMS membrane	56
Figure 4.7	Infrared spectrum of 5 wt. % PDMS membrane	57
Figure 4.8	Infrared spectrum of 8 wt. % PDMS membrane	58
Figure 4.9	Infrared spectrum of 10 wt. % PDMS membrane	59

LIST OF SYMBOLS

^{o}C	Degrees celcius
^{o}F	Degrees Fahrenheit
$\alpha_{i/j}$	Selectivity of pure gas
µm	Micro meter
Δp	Pressure drop
€	Euro currency symbol
A	Area
kg	Kilogram
kJ	Kilo Joule
kPa	Kilo Pascal
K	Kelvin
l	Thickness of membrane
m^2	Unit area, meter square
m^3	Unit volume, meter cubic
MPa	Mega Pascal
P_{us}	Upstream pressure
P_{ds}	Downstream pressure
Q_i	Gas flow
wt. %	Weight percentage
W	Watt

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
CA	Cellulose Acetate
CCS	Carbon dioxide Capture and Storage
CE	Cellulose Esters
CH_4	Methane
CN	Cellulose Nitrates
CO	Carbon monoxide
CO_2	Carbon dioxide
EPA	Environmental Protection Agency
FTIR	Fourier Transfer Infrared
GPU	Gas Permeation Unit
H_2	Hydrogen
H_2O	Water
IPCC	Intergovernmental Panel on Climate Change
N_2	Nitrogen
O_2	Oxygen
PA	Polyamide
PAN	Polyacrilinitrile
PDMS	Polydimethyl siloxane
PE	Polyethylene
PES	Polyethersulfone
PMMA	Polymethyl methacrylate
PP	Polypropylene
PS	Polysulfone
PTFE	Polytetrafluoro ethylene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
SEM	Scanning Electron Microscopy
STP	Standard Temperature Pressure
TFC	Thin Film Composite

CHAPTER 1

INTRODUCTION

1.1 Background of Research

In 2007, Intergovernmental Panel on Climate Change (IPCC) indicate that during 21st century the global surface temperature is likely to rise a further1.1 to 2.9 ^{o}C (2 to 5.2 ^{o}F) for their lowest emissions scenario and 2.4 to 6.4 ^{o}C (4.3 to 11.5 ^{o}F) for their highest. It shows that the average temperature of Earth's atmosphere and oceans is rising and this situation referred as a global warming. The main root to this unequivocal warming of the climate system is certainly because of increasing in concentration of the greenhouse gasses produced by human activities such as deforestation and burning fossil fuels. The challenging issue is to controlling the greenhouse gasses like carbon dioxide (CO_2) emission to atmosphere.

Carbon dioxide Capture and Storage (CCS) is found as a promising way of reducing the emission of carbon dioxide and at the same time it is mitigating the contribution of fossil fuel emissions to global warming. The conventional process of CCS is by reversible solvent absorption which is based on capturing CO_2 from large point sources and storing it in such a way that it does not enter the atmosphere. However, capturing and compressing CO_2 consume high energy and it would increase the fuels need of a coal-fired plant and this cost will increase the cost of energy from a new power plant. It shows that the conventional process of CCS is less economical.

Therefore, gas membrane separation seems to be more economical process. Membrane separation operates without heating and is energetically lower than conventional thermal separation process. This type of separation decently physical and both permeate and retentate can possibly use. Its energy efficiency and simplicity is most attractive to CO_2 capture. In order to obtain a pure stream of CO_2 and attain the compact membrane facility, the membrane used must be high in term of selectivity and permeability.

Variety types of membrane can be used and this study will focused on the polymeric membrane for some purpose. The properties of the polymeric membrane makes it is well-suited to the low temperature application. The morphology of the membrane also can easily determine the permeability and selectivity of the membrane. The utmost important is it is easy to manufacture.

Besides, previous researchers believe that significant advances in traditional polymeric membrane will be difficult to attain because we are currently approaching the limit of the technology. The trade-off between selectivity and permeability is based on traditional structure properties relations of polymeric materials. This upper bound still defines the properties of all truly solution process able polymeric materials today. This phenomenon had leads for the growing interest in the development of gas separation membranes based on materials that provide better selectivity, thermal stability and chemical stability than those already exist (Aizan *et al.*, 2006).

1.2 Problem Statement

In gas separation process, the main key of the good performance using membrane is depends on the permeability and selectivity of the membrane. The properties of the membrane material are the main factors in this separation process. Polymers such as polyamide, polidimethylsiloxane (PDMS) and polyvinylidene fluoride (PVDF) were known as good materials in producing membrane. However, previous study found that a pure polymer such as PDMS is a low selectivity material. The limitation in achieving the high selectivity and permeability membrane is the great challenge in producing membrane for a gas separation. The thin film composite (TFC) membrane based on PDMS and PVDF is considered to be one of the practical approaches to overcome the limitation. Therefore, the selection of the proper material needs a proper attention in order to produce the good membrane.

1.3 Research Objectives

The main purpose of this study is to perform the high performance in separate CO_2 from CH_4 in biogas purification by using PDMS/PVDF TFC membrane. The objectives of this study are:

1) To produce TFC membrane based PDMS/PVDF
2) To study on performance of TFC membrane to separate CO_2 and N_2.
3) To characterize the TFC membrane.

1.4 Scope of Research

This study has focused on several scopes in order to achieve its objective. The scopes are as follows:

1. Production of the TFC membrane based PDMS/PVDF.
2. Study the performance of the TFC membrane in term of permeability and selectivity.
3. TFC membrane characterization using Scanning Electron Microscopy (SEM) and Fourier Transforms Infrared (FTIR)

1.5 Significance of Research

Thin film composite membrane is one of the most effective membranes for gas separation because of its asymmetric and porous structure. The combination of the advantages of PDMS as the coating layer and PVDF as support layer in this membrane is the reason for its high performance. Besides, membrane separation process did not require any latent heat. Thus, it could save lost energy consumption. Membrane separation process is an environment friendly process since this process produces no waste that could harm the earth. Its simple process makes it is more economical to use membrane than other method for gas separation.

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane

2.1.1 Definition

A membrane can be defined as a thin layer of material that used as a selective barrier between two bulk phase either homogenous or heterogeneous phase. It will allow some component passes through and it will retain some.

2.1.2 Principal

The principal of membrane separation is some components of the feed are transported through a thin film membrane and some will be retained. In gas separation, membrane acts as filter to separate one or more gases from feed mixture and generate specific gas rich permeate. The membrane performance is identified in term of permeability and selectivity.

Permeability is a measurement of the quantity of fluid that passes through the membrane per unit area of membrane per unit time. It is linearly depends on the permeability and the driving force and inversely depends on the membrane thickness. That mean, the flux will be greater when the membrane is thick and at higher permeability and driving force. Selectivity can be defined as a preference of the membrane to pass one species and not another (Stookey, 2001). The schematic principal of membrane in separation process is illustrated in the Figure 2.1 below.

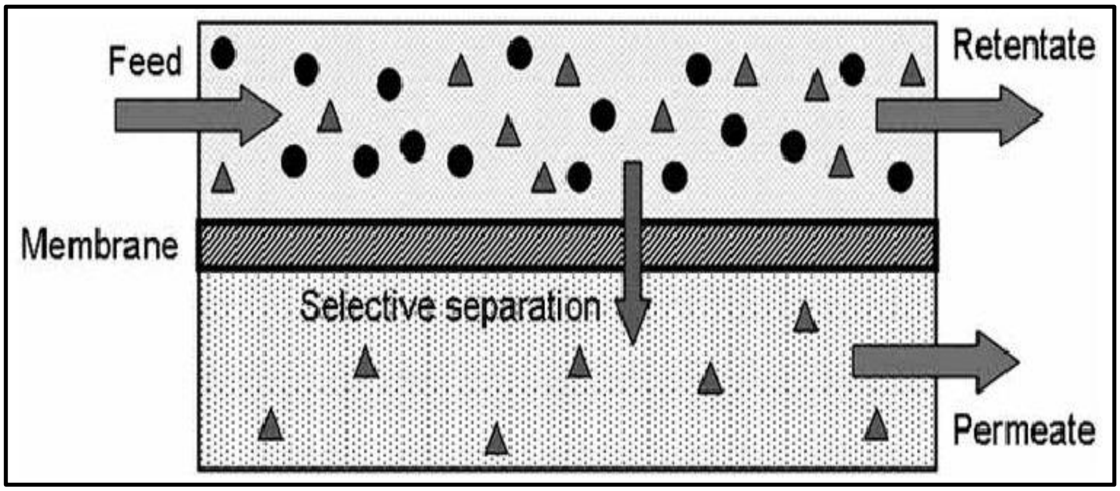

Figure 2.1: Schematic diagram of membrane separation (Sandra *et. al*, 2008)

There are two main types of flow; dead-end flow and cross-flow. The direction of dead-end feed flow is normal to the membrane surface. It is easy to implement but not preferred because of extensive membrane fouling and concentration polarization. The concentration polarization (particle backflow) was build up from the fouling membrane where the driving force was higher. It intends to the increasing of non-permeating species on the feed side with time. This means that, decrement in the concentration of the permeating species in the feed side is reducing the driving force and transportation of particle through the membrane.

In contrast, the cross-flow membrane process is the preferred one due to its tangential flow to the membrane surface. Further downstream, the retentate is removed and on the other side, the operation which is permeating flow is tracked. There is four cases of cross-flow operation which is co-current, counter-current, cross-flow with perfect permeate mixing and perfect mixing operation. The types of the feed flow are shown in the Figure 2.2 below.

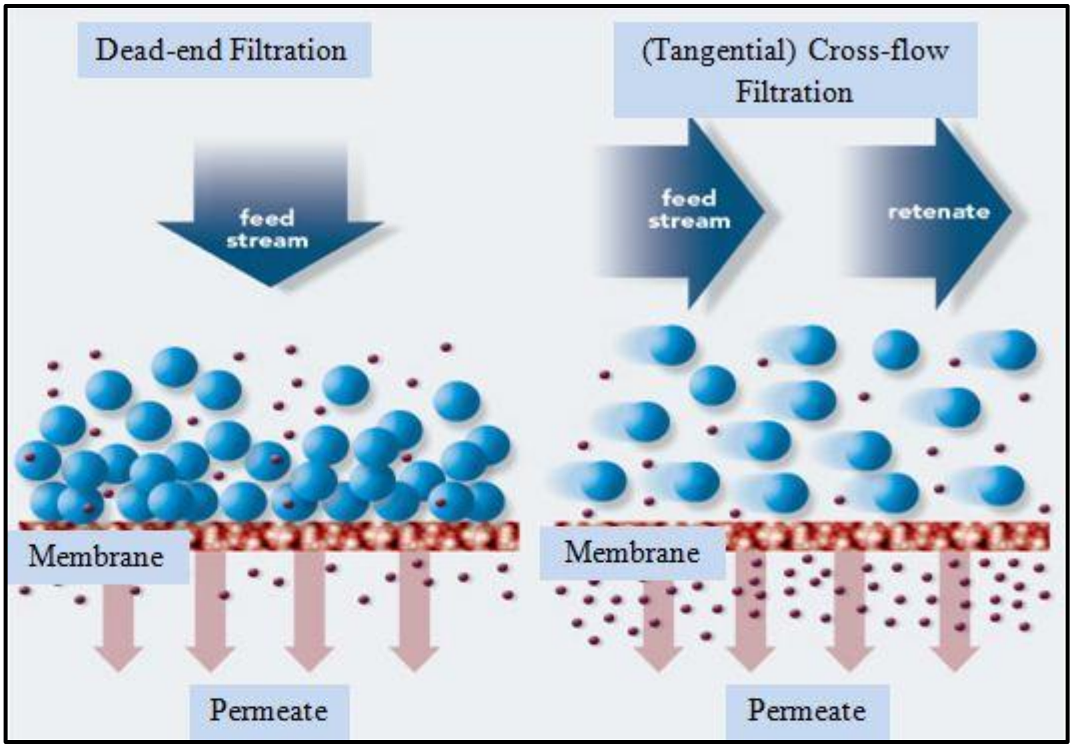

Figure 2.2: Feed flow illustration

2.1.3 Types of membrane

Generally, there are two types of membrane which is biological membrane and synthetic membrane. A biological membrane is a selective barrier layer that is around the cell which consists of lipid bilayer with embedded protein. The lipid and protein composition in this membrane is different due to its types.

In the other hand, the synthetic membrane was produced from organic or inorganic materials. A membrane from inorganic materials such as silicon carbides, aluminium oxides or zirconium oxides is resistant to the strong solvent action and chemically and thermally stable. One of the popular membranes that used in the separation industry is a polymeric membrane.

A polymeric membrane is an organic synthetic membrane that can selectively transfer certain chemical species over others. Common polymers that commonly used in membrane synthesis are cellulose acetates (CA), cellulose nitrates (CN), cellulose esters (CE), polysulfone (PS), polyether sulfone(PES), polyacrilonitrile (PAN), polyamide (PA), polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polyvinylchloride (PVC).

Another type of membrane is micro porous membrane. This type of membrane is generally made by applying 1 to 3 thin layers to a porous support. The porous support can be in flat sheets, disks or tubes and can be either ceramic or metallic. Meanwhile the microporous layers are generally metal oxides and are often silica. Microporous membrane usually applied for coal gasification, reformed natural gas and in high-temperature electrolysis.

Homogenous dense and asymmetric membranes are also the main type of membrane that usually used. Homogenous dense membrane usually prepared by solvent evaporation from the solution or by extrusion of the melted polymer. This type of membrane is practical when it is made from highly permeable polymers like silicon.

2.1.4 Membrane structure

Membranes can be classified according to their morphology. The morphology of the membranes is illustrated on the Figure 2.3.

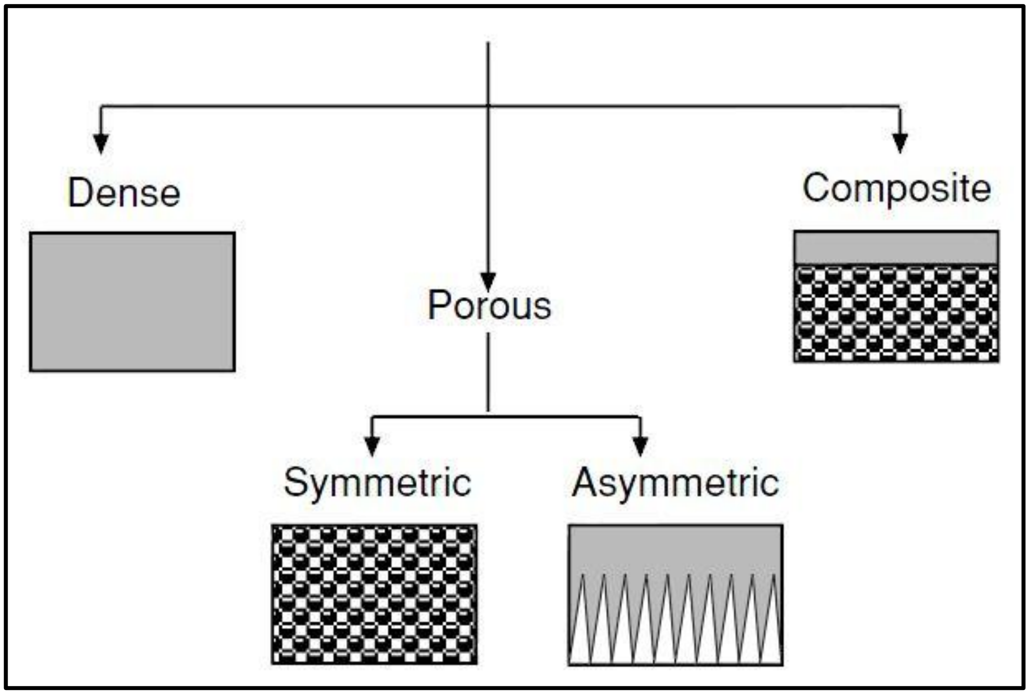

Figure 2.3: Membrane classification according to morphology (Nunes *et al.*, 2001)

A dense membrane usually prepared from highly permeable polymer in a minimal thickness in order to give the mechanical stability to the membrane. Therefore, most of application used porous membrane or composite membrane which combines the dense layer at the top and porous membrane at the bottom.

A symmetric membrane have a constant diameter pores and it is resistance to mass transfer due to its thickness. In contrast, asymmetric membrane has a different pore sizes between the top surface and the bottom one. The size difference unable the particle to pass through the membrane and the plugging must be avoided. One best solution to this problem is by using composite membrane. The top layer of the composite will be the membrane selectivity to the porous one at the bottom. The bottom layer has high porosity and high thickness.

2.1.5 Mechanism of membrane

Mechanism of membrane in separation process can be divided into:

i. By size

   Macropores, mesopores and micropores are three terms that defined the pore sizes in membrane for microfiltration, ultrafiltration and nanofiltration membrane. This type of membrane is used to removed contaminants based on sized.

ii. Different in solubility and diffuse of materials

   This type of mechanism is based on the diffusion of solute and solvent. The membrane has a small pores and only solvent passes through it by sorption-diffusion method. A composite of homogenous film is the good example.

iii. By charge

   This mechanism used in an ion exchange membrane where the same charge ion is excluded in the same phase. It is practically used in electrolytic cell separator.

There are three types of mechanism used in the gas separation membrane; Knudsen diffusion, molecular sieving and solution-diffusion. In Knudsen diffusion mechanism, the component of the gas is separated according to the difference in mean path of the gas molecules. In contrast, the gas is separated based on the diameter size of molecule in molecular sieving mechanism. A solution-diffusion happen when permeates dissolved in the membrane material and separation is achieved because of differences in amount of material dissolves in the membrane and rate of material that diffuse. Figure 2.4 below shows the mechanism in gas separation.

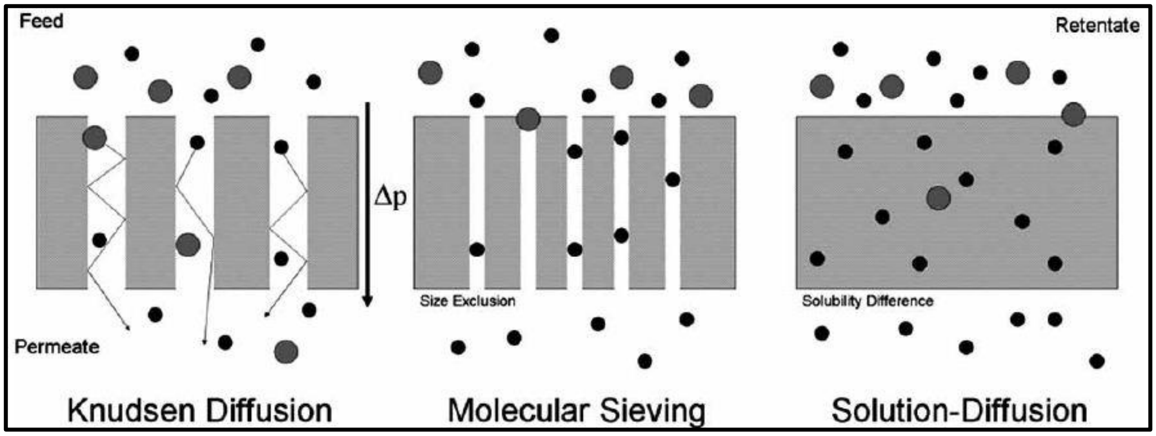

Figure 2.4: Illustrations of membrane mechanism (Sandra *et al.*, 2008)

2.2 Membrane Process

Based on previous study, Aizan *et al.*, 2006 claimed that the membrane separation process is characterized by several aspects. There are:

- Separation goal
- Nature of species retained (size of the species)
- Nature of species transported through membrane, electrodylasis or volatile
- Minor or major species of the feed solution transported through membrane
- Driving forces
- Phase of feed and permeate stream
- Mechanism for transport/selectivity

The membrane separation processes are summarized in the Table 2.1 and characterized based on the mechanism used; feed stream, trans membrane driving force and its application in the industry.

Table 2.1: Membrane separation process (Aizan *et al.*, 2006)

Separation process	**Separation mechanism**	**Feed stream**	**Typical trans membrane driving force**	**Example of industrial use**
Microfiltration	Sieving	Liquid or gas	Δp<10-21	Processing of corn stillage streams, concentration of emulsions, cell suspension concentration
Ultrafiltration	Sieving	Liquid	Δp<50psi	Auto-paint recovery, microemulsion oil recovery, biomolecule and virus separation from aqueous stream
Dialysis	Sieving and sorption-difusion	Liquid	Δp<0 to small Δp sometimes	Hemodialysis primarily
Reverse osmosis	Sorption-difusion	Liquid	Δp<often to overcome osmotic pressure, so Δp-Δπ>0, usually<1500 psi	Water desalination, wastewater treatment
Pervaporation	Sorption-difusion	Liquid	Δ(fugasity of i) set by fed liquid mole fraction and permeate vacuum	Dehydration of organic stream and removal of trace organics from aqueous streams
Gas and vapor permeation	Sorption-difusion	Gas and vapor	Δ (fugasity of i) usually equal to partial pressure difference, Δpi typically<120 psi	Separation of O_2/N_2, H_2/CH_4, CO_2/CH_4, H_2/N_2, H_2/CO, H_2O/CH_4, and organic vapors from air

2.3 Membrane Module

Membrane module can be defined as the building block of the membrane and generally its configuration can divided into two; flat and tubular.

2.3.1 Plate and frame module

This plat membrane is placing parallel to each other with a spacer plate that separates the feed flows. In order to use the membrane surface as efficiency as possible, the stop disc was used to improve the flow pattern. It helps in reducing the tendency of the flow to moves at fixed pathway. The packing density of this module is around 100-400 m^2/m^3 (EPA, 2005). Figure 2.5 below display the plate and frame membrane module.

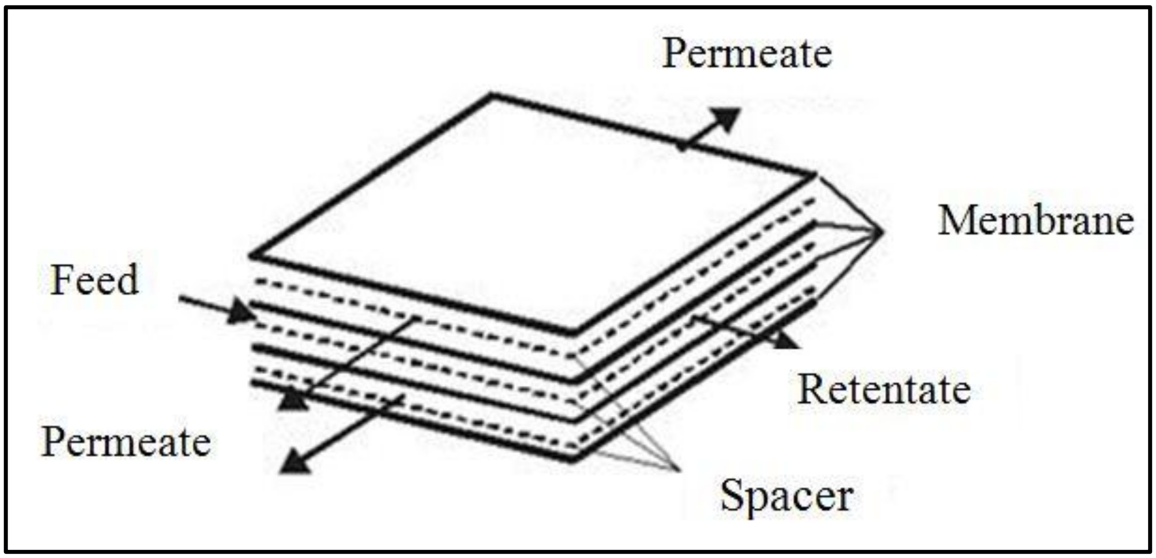

Figure 2.5: Schematic diagram for plate and frame module (EPA, 2005)

2.3.2 Spiral-wound module

Spiral wound module is a two layers membrane that placed onto a permeate collector fabric and wrapped around a central placed permeate. It makes the cylinder density is high, 300-1000 m^2/m^3. The feed flows in an axial direction while the permeate run in radial direction towards the centre of cylinder. It should be placed at the moderate high to prevent the plugging happen. The spiral wound membrane module shown in the Figure 2.6.

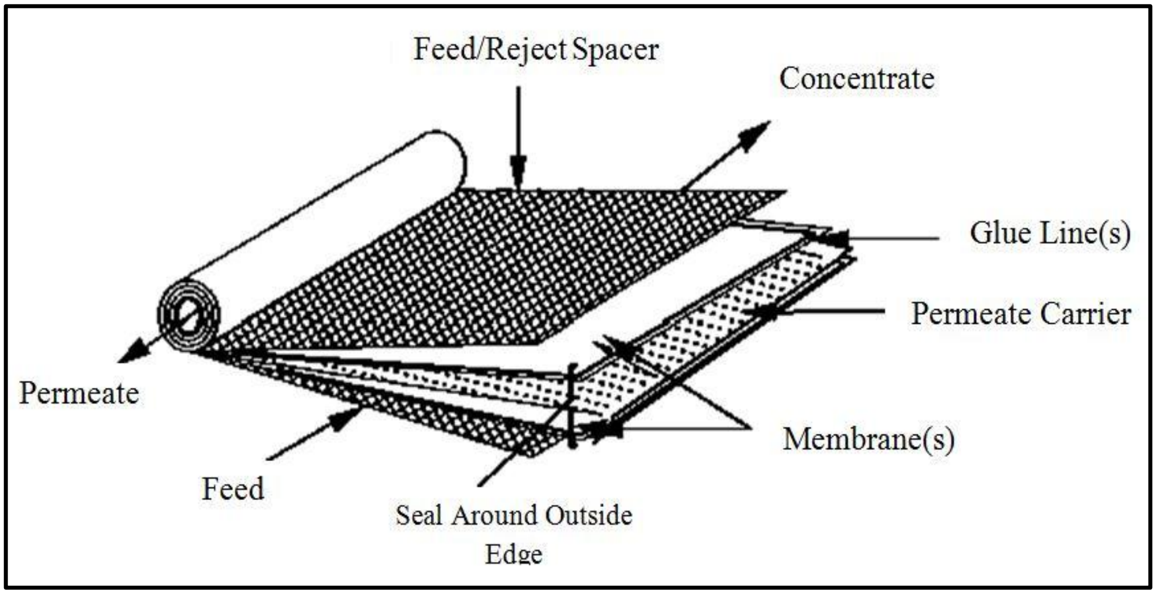

Figure 2.6: Spiral wound membrane module (EPA, 2005)

2.3.3 Tubular Module

The supporting material is placed inside a 5 to 15 mm diameter tubular tube. Its bigger size makes the density quite low and plugging seems not happen. The attachment of the supporting materials is not strong enough and makes the feed flow in the centre of the membrane tube and the permeate flow outside the tubular. Figure 2.7 shows the module for tubular membrane.